ELECTROLYSIS: A NEW POSSIBILITY FOR "IN SITU" Fe-Mn ELIMINATION

by

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Abstract

Electrolysis, one of the possible methods of "in situ" Fe-Mn elimination, is not economical under common hydrogeological conditions.

Since in Hungary the hydrogeological conditions do not allow a proper use of the oxygene input method, a detailed study of other methods had to be done to examine the possibilities of their individual and even combined use.

In this study the problem has been approached through experiments on small samples, followed by tests done under laboratory conditions but in industrial dimensions (electrode distance = 6 m) to get prepared for the frothcoming tests at industrial level.

Purpose and scope

The laws of electrolysis were laid down by Faraday in the 19th century, and they soon became widely used in galvan technology. The results of our study prove that under seepage conditions the theoretical and "in vitro" connections differ from each other.

In our experiments we followed both the direction and the efficiency of cathodic processes step by step from the water filled glass vessel to an aquifer, made of fine sand.

The examined equation and parameters are given using the formula:

$$G = A_e \times I \times t \times n$$

where

G	=	weight of material gained by electrodeposition
A_e	=	electrochemical equivalent weight (in case of $Fe^{2+} - Fe^{O}$, this value is 1.042)
I	=	current intensity
t	=	time
n	=	cathodic efficiency.

The aim of "in situ" Fe-Mn elimination is to bring the dissolved $Fe(HCO_3)_2$ and $Mn(HCO_3)_2$ into solid state and, if possible, to remove them. To achieve this, there are two optional electrolytic ways, namely

i	:	removal of the elementary Fe and Mn on the cathode
ii	:	oxidation of the Fe^{2+} to Fe^{3+} on the anode, where it hydrolyses and becomes solid.

This paper discusses the effects of different conditions on elestrodeposition of metals from a solution.

Deposition voltage	:	0 – 48 volts
Current intensity	:	0 – 300 ampers
Electrodes,		
cathode	:	spectroscopically pure graphite bar
anode	:	graphite or iron bar
Effective electrode surface	:	2 x 1386 mm^2
Electrolysis tank	:	250 x 250 x 450 mm glass vessel.

Experimental variables: voltage, current intensity, time, Fe-Mn content, media (water, gravelly-, coarse and fine sand), grain sorting, clay and humin acid content.

Experimental testing

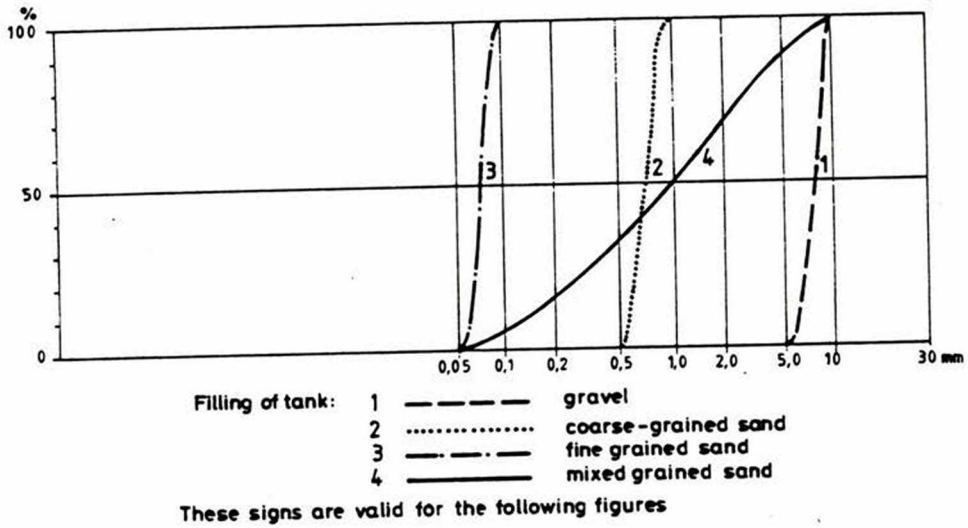

Fig. 1. Investigated granulometric composition

Experiment A, Fig. 2.

Experimental conditions: voltage 2 V, current density 4330 A/m^2, time 6000 sec, surface of the graphite electrodes 2 x 1386 mm^2, electrolite concentration range within 0.5 – 2.5 g/l.

Theoretically, in case of 100 percent electric and cathodic efficiency, it would be separated:

$$G = 1.042 \times 0.1386 \times 43.3 \times 1.67 \times 1 = 10.44 \text{ g Fe}$$

In practice, the electro-separated amount is 25% of the counted value, due to decrease in efficiency.

In agreement with our other experiences, along with the decreasing porosity in clastic aquifers, the speed of chemical reactions also decreases rapidly.

During the given time of experiment and in case of 0.5 – 2.5 g/l iron concentration the amount of separated material does not depend on the concentration of the solution.

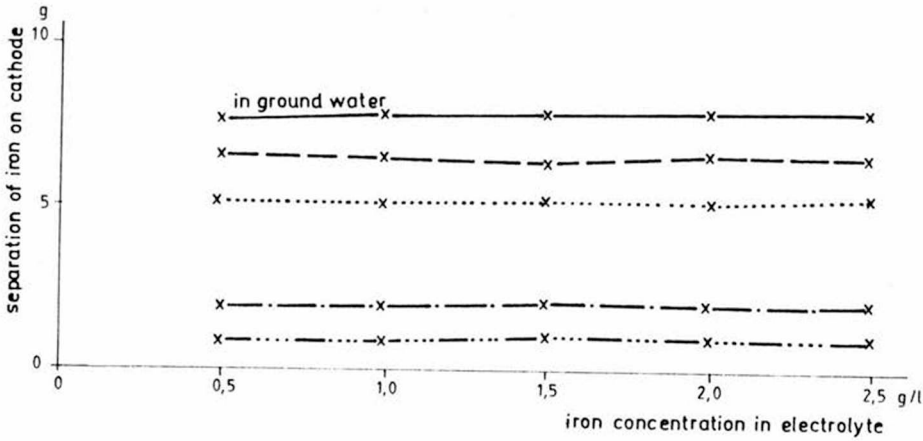

Fig. 2. Connection between iron concentration in electrolyte (0,5-2,5 g/liter) and separation of iron on cathode

Experiment B, Fig. 3.

Here the conditions are identical with those of experiment A, except for the concetration that was reduced to 0.5 – 2.5 mg/l, i.e. to values characteristic of reservoirs storing riverbankfiltered waters.

The measured results proved that the electrically deposited amount is close to the theoretical maximum, both in water or gravels and coarse sands but separation is much poorer in substances of fine or mixed grain size distribution.

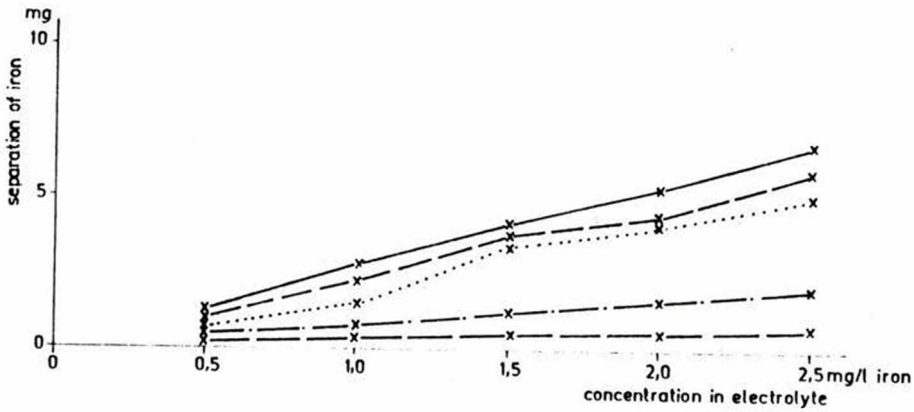

Fig. 3. Connection between iron concentration in electrolyte (0,5-2,5 mg/liter) and spearation of iron

Experiment C, Fig. 4.

The clay content was changed from 0 to 5%, while the Fe concentration remained 2 mg/l.

The efficiency of the electric deposition increased with the clay content in water and in gravel deposits, however in the latter case to a lesser extent. The amount of separated Fe decreases parallelly with grain size diminution and clay minerals are even more holding back the diffusion process.

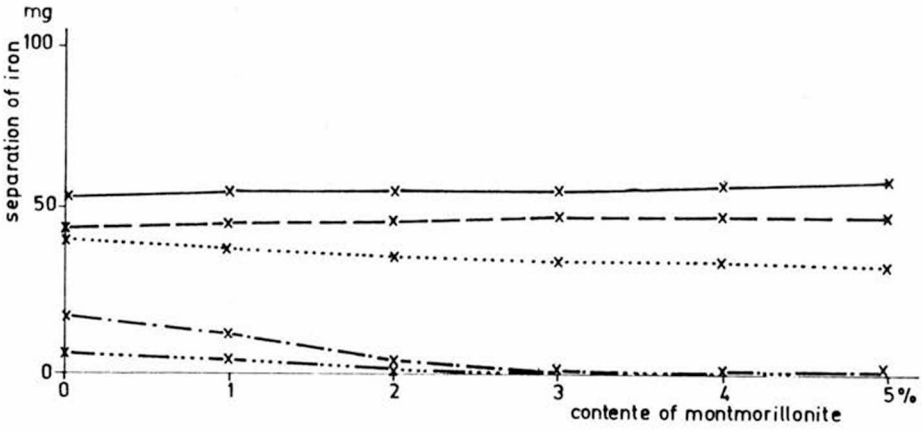

Fig. 4. Connection between content of montmorillonite and separation of iron

Experiment D, Fig. 5.

We added 5% humin acid to an electrolyte containing 2 mg/l $Fe(HCO_3)_2$ to investigate the effects of protecting colloids. The examination of the "sub-terra" method proved that oxygene rich water has little effect if the ground water contains humin acid, because it forms a protecting colloid around the Fe^{2+} ions. The measured values scattered within a very large scale even after repetition, so at *Fig. 5.* the average of the 3 series of measurements can be seen. The shape of the curve shows that the protecting colloid remained active during elecrolysis.

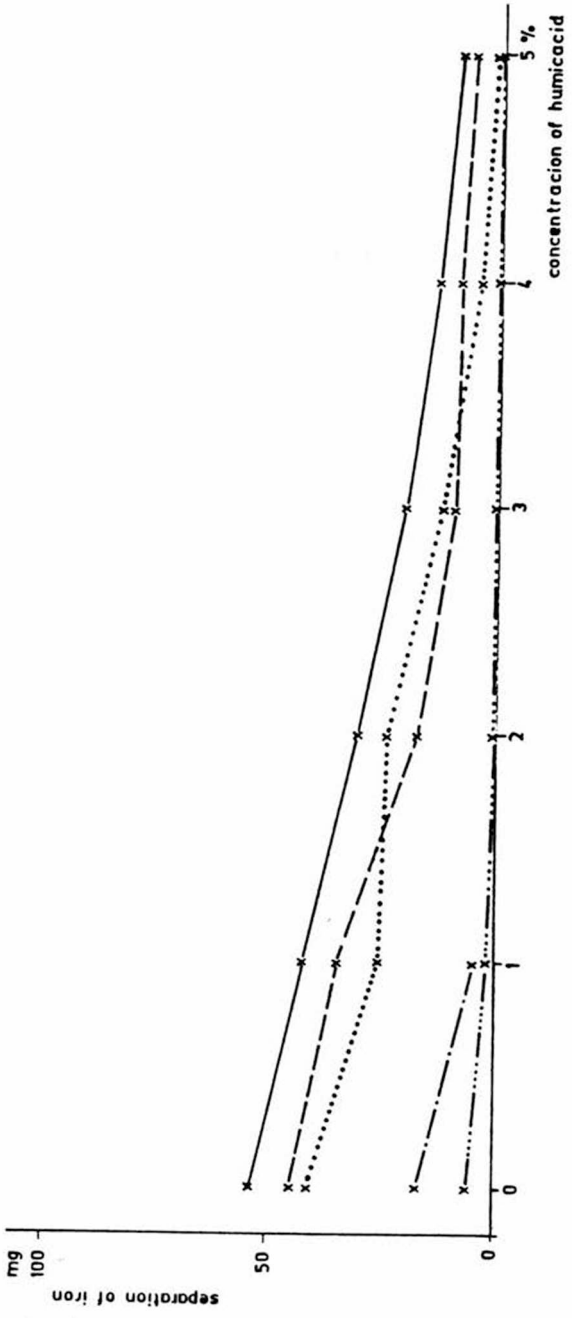

Fig. 5. Connection between concentration of humic acid and separation of iron

Experiment E, Fig. 6. and 7.

In this experiment we investigated the effects of time on electrodeposition both in laboratory and in industrial tests (electode distance = 0.4 and 6 m).

The speed of the reactions decreased remarkably with grain size as shown by data in *Fig. 6.* In case of gravelly and coarse sandy aquifers the reaction speed is just acceptable for economical reasons, but it is insufficient in fine sand and poorly sorted media.

Fig. 7. Shows that if elecrode distance increases up to 6 m the drop in reaction speed is more remarkable and only gravelly aquifers meet the economic demands.

If we compare *Fig. 6.* and *Fig. 7.* it can be seen that there is no direct relationship between grain size and reaction speed.

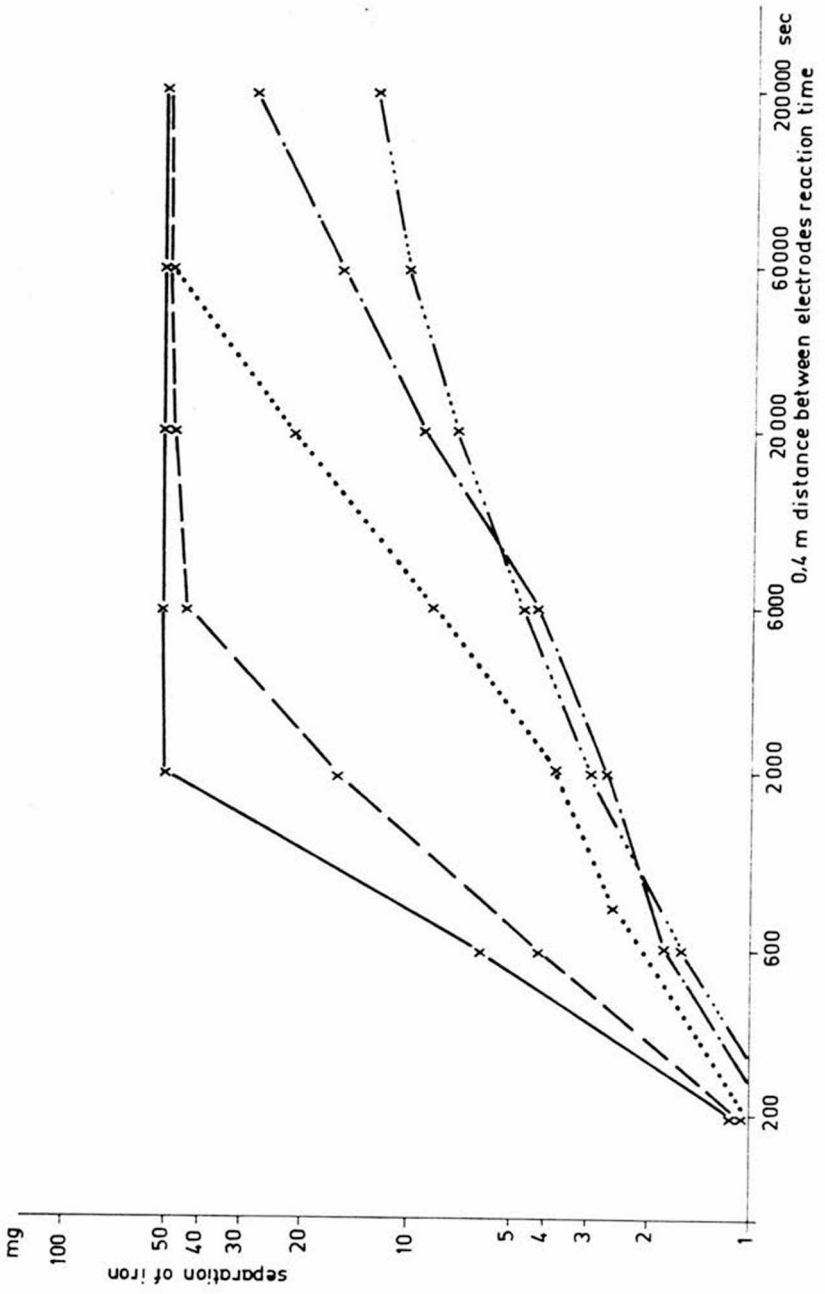

Fig. 6. Connection between reaction time and separation of iron

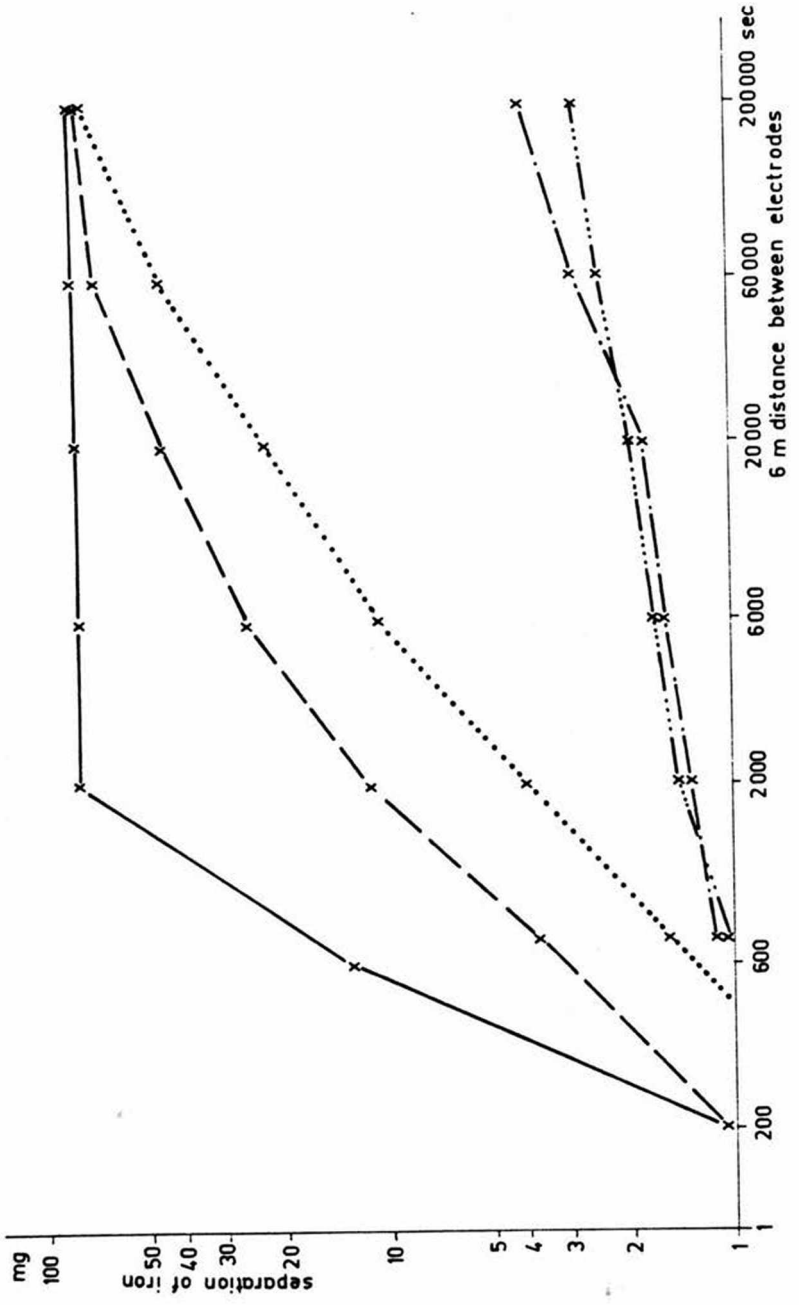

Fig. 7. Connection between reaction time and separation of iron

Experiment F, was planned to investigate this matter. Fig. 8.

In water the electode distance has no direct effect on reaction speed but in the conditions of seepage the increase of electrode distance causes a considerable drop in reaction speed.

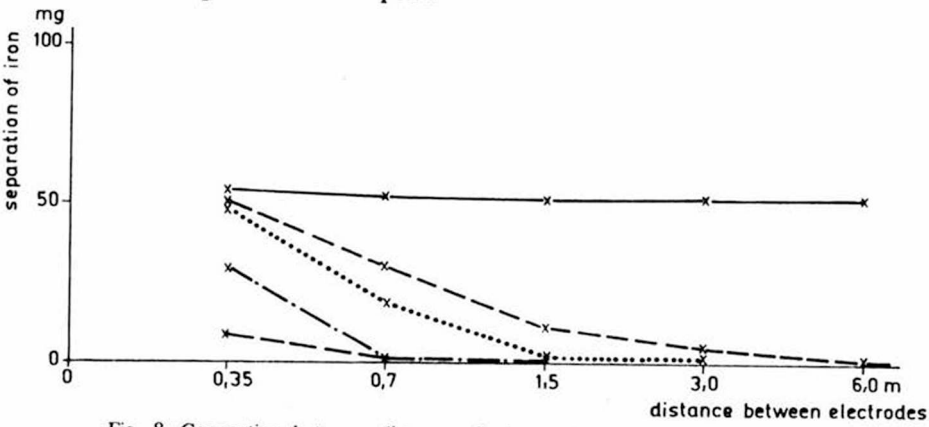

Fig. 8. Connection between distance of electrodes and separation of iron

Experiment G, Fig. 9.

It was necessary to determine the optimum operation voltage without proper theoretical bases, because no kind of constant of chemical balance or "in vitro" relation is applicable to the concrete chemistry of the ground water.

In experiment G the operating votlage was increased until instead of Fe deposition bubbles of hydrogene appeared on the cathode, showing the increased speed of water decomposition. While an iron cathode can adsorb a small amount of H_2, a graphite electrode can not and the appearing bubbles show immediately the H_2 formation. In galvan technology handbooks the next overvoltage values can be found for H_2 formation:

Table 1.

case of spongy Ni cathode	:	0.05 V
smooth surface Ni cathode	:	0.14 V
Fe cathode	:	0.17 V
and for O_2 formation on the anode:		
case of spongy Ni anode	:	0.05 V
smooth surface Ni anode	:	0.12 V
Fe anode	:	0.24 V

Data, shown in Table 1, indicate that the surface of the electrodes play a significant role in electrodeposition. Because of the elctrodeposited spongy Fe, the electrode surface can hardly be properly defined, and this causes an additional uncertainity in the experiment. The numbers of the water samples on *Fig. 9.* (I. to X.) do not mean logical order, because changes in the chemical nature of the individual ground water samples did not allow us to set up any kind of order with attention of every component. Only a slight relationship can be found between resistivity and electrodeposition, which can be explained but has no special importance.

These experiments prove that there is no proper way to estimate theoretically the maximum value of the operating voltage, it differs in every individual case. It is possible that is also changes during electrodeposition because of the polarisation of the electrodes.

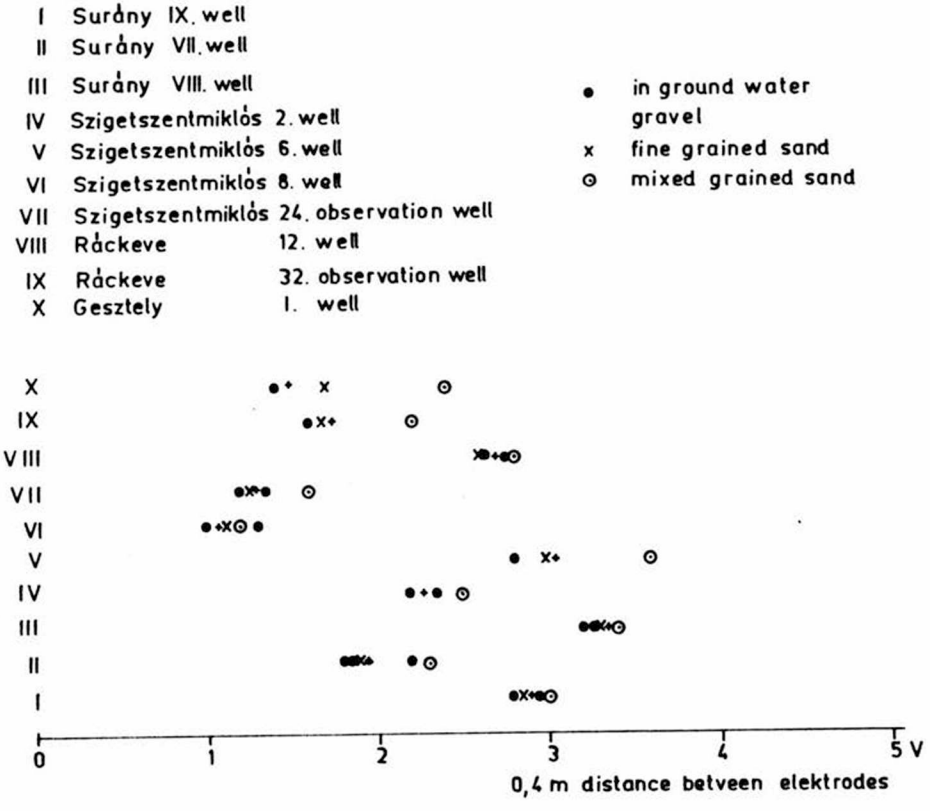

Fig. 9. Operating voltage at the different samples

Experiment H, Fig. 10.

In galvan technology current density defines the quality of electrically deposited metal, so in plating baths it is always kept constant. When elecrodeposition is used for the elimination of the Fe and Mn content of ground waters, only the amount of the deposited metal is important. The next series of experiments were done to determine the optimum value of current density. The next problem, which has already been mentioned, was that the electrode surface is well defined only at the beginning of the experiment and the deposited more or less spongy Fe makes the surface undefinable.

To avoid this problem the time of experiments was reduced.

Fig. 10. proves that current density has no optimum level but above 2000–3000 A/m^2 the slope of the curve decreases, which can be evaluated as the point of the maximum efficiency for industrial tests.

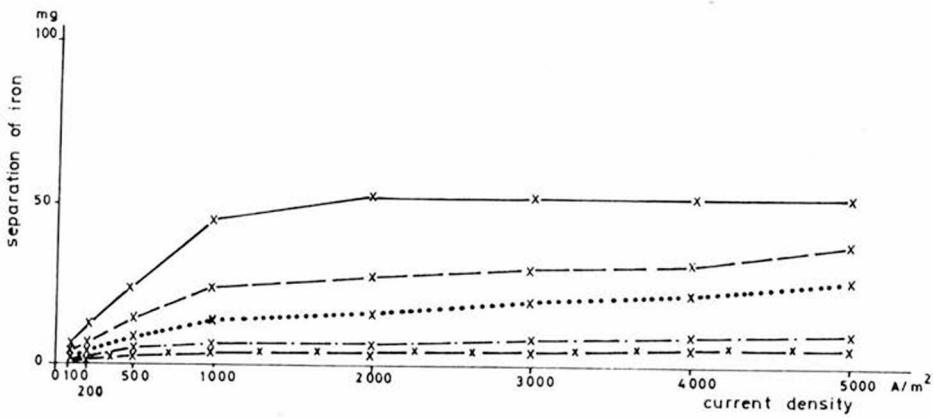

Fig. 10. Connection between current density and iron separation

Experiment I, Fig. 11.

As previous experiments let is suppose the "in situ" application of the electrolysis alone is not economical. In the next experiment electrolysis was combined with the batch-type "sub-terra" method.

There are several ways to express the efficiency of the "sub-terra" method, in this case the rate of the produced and recharged oxygene-rich water seemed to be the best. *Fig. 11.* shows that the producing/recharging rate improved remarkably, and this fact suggests further economical calculations.

Experiment J,

As there are continuous in situ Fe-Mn elimination methods too, an experiment was planned to combine the two methods under the conditions of seepage. As the required equipment was rather complex and the measurements scattered within such a large range that this application needs further investigation. The average results of the preliminary experiments are encouraging.

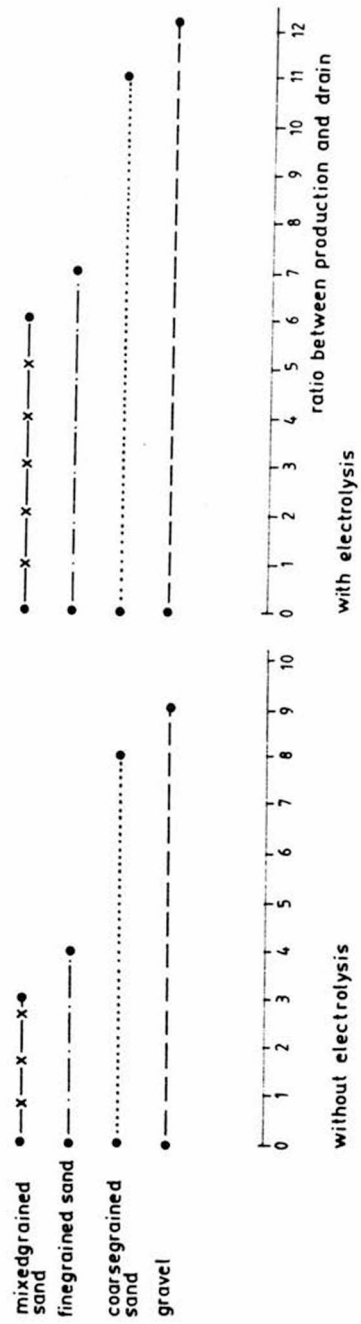

Fig. 11. Ratio of production and drain at different granulometric compositions

Conclusions

The efficiency of the above described cathodic metal deposition method is proportional to grain size and porosity, and varying within a range of 20-90%. Compared with other "in situ" Fe-Mn elimination methods, both the factors working against efficiency (clay minerals, humin acid content), and their effects are the same.

When estimating the required depositional voltage several individual experiments have to be done because of the complexity of numerous influencing factors. The range of the optimal current density is within 2000–3000 A/m^2. Electrolysis can be economical only as a complementary of the "sub-terra" batch-type "in situ" Fe-Mn eliminiation method. The combined use of electrolysis and "sub-terra" methods needs further testing. The anodic processes also require a detailed investigation because this side process should also increase the efficiency of the method.

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